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Separation and identification of organic and organometallic compounds by use of a liquid chromatography–particle beam-glow discharge mass spectrometry combination

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Abstract

Evaluation of the particle beam glow discharge mass spectrometry (PB-GDMS) system as a detector for liquid chromatography (LC) is described for the analysis of polycyclic aromatic hydrocarbons, steroids, selenoamino acids, and alkyllead compounds. A particle beam interface is used to introduce analyte species from the LC into a glow discharge source for subsequent vaporization and ionization. Mass spectra display classic EI fragmentation patterns for the organic compounds, as well as elemental and molecular information for the organometallic compounds. Chromatographic separations display good temporal correlation between UV and PB-GDMS detection modes. Detection limits for Pb in lead nitrate, triethyllead, and triphenyllead fall in the sub-ppb (ng) range.

Keywords: Particle beam glow discharge mass spectrometry; Detection, LC; Organometallic compounds

1. Introduction

One of the primary limiting factors in environmental and biological research is a lack in spectrochemical (i.e., elemental analysis) methods, which are capable of providing detailed chemical speciation information [1]. There are various levels of information which are required for proper assessment of trace element species: total elemental composition, oxidation states, and bound ligand/molecule identification [2]. While chromatographic methods exist for separating the various ''species'' in which a trace metal can exist in an environmental or biological matrix, the limiting factors are the means of identifying the components. At present, an ''either/or'' situation exists in terms of detecting and identifying the metal or the entire molecule with a single detection scheme [3].

The need for oxidation state information is met in the elemental analysis (atomic spectrometry) community through the interfacing of liquid chromatography (LC) to inductively coupled plasma atomic emission and mass spectrometry (ICP-AES-MS) instruments [4–6]. While the elemental sensitivity of ICP-MS for chromatographic separations is tremendous, the fact remains that these approaches do not

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provide the truly desired ''molecular'' speciation information, as these plasmas rely on the total dissociation of any analyte species down to the atomic level.

In cases of organic/molecular species identification in liquid samples, there exist a large number of candidate detection methods involving mass spectrometry. Over half a dozen distinct ionization methods/sources are available [7]. The choice of which ion source to employ depends on the target compound class and liquid matrix identity. The complexity of this challenge increases when the identification of inorganic species is also required. At present, commercially available ''organic'' ion sources (electron impact and chemical ionization) are not readily applicable to the ionization of atomic ions, as the cross sections for these processes are quite low. Electrospray ionization (ESI) has demonstrated capabilities to produce molecular mass spectra from inorganic ions, with the possibility of obtaining elemental mass spectra through collisional dissociation of the complexes in the ion sampling region [8]. Unfortunately, the electrospray process is not readily compatible with the ionization of nonpolar analytes, and its freedom from matrix effects and quantitative powers are still very much in question.

Low-pressure, low-power glow discharge (GD) ion sources present some very interesting possibilities for simultaneous organic and inorganic analyses because of the mechanisms by which they create positive and negative ions. Ionization in the glow discharge is documented in the atomic spectroscopy literature to occur by three general mechanisms: electron impact (EI), Penning-type, and charge-exchange collisions [9]. Studies performed in the ionization/analysis of molecular species also point to electron attachment (EA) and chemical ionization (positive and negative) as prominent ionization pathways [10–15]. Based on a number of applications of glow discharge mass spectrometry (GDMS) in both the elemental and molecular MS arenas, the glow discharge could be a universal ionization source for atomic and molecular, as well as polar and nonpolar, species. In practice, introduction of solution eluents into the GD source calls for the use of transport interfaces of the sorts used in LC–MS applications to deliver solvent-free analytes to the low pressure plasma [16]. For this reason, this laboratory has investigated the use of a particle beam (PB) interface for sample introduction into glow discharge atomic emission [17–20] and MS sources [21].

Particle beam interfaces were originally developed for the specific case of wishing to perform LC–MS of small molecules by way of electron ionization [22–24]. As such, PB-LC–MS would enjoy the benefit of yielding mass spectra which were searchable in existing databases [22]. In simplest terms, a particle beam LC–MS interface includes a means of nebulizing and desolvating the chromatographic eluent, then delivering the resultant dry solute particles to the ion volume through a multistage momentum separator. Likewise, the use of the PB interface for GDMS means that residual vapors of the mobile phase do not carry over into the ionization environment. Therefore, the operation of the GD source is not compromised and complicating secondary reactions between analytes and vapor species are alleviated. Other advantages of the PB interface are its mechanical and operational simplicity, compatibility with a wide range of solvent polarities and flow-rates, as well as accepting LC eluents while maintaining natural chromatographic characteristics such as retention/elution quality.

The application of the PB-GDMS technique for the analysis of liquids was recently explored for the case of simple elemental and organic samples [21]. An investigation of the influences of discharge operation parameters, as well as general characteristics of the approach were demonstrated for the caffeine molecule, with a resulting detection limit of 2.7 ng and less than 5% relative standard deviation (RSD) for triplicate 500 ppm injections with a 200-μl loop [21]. Subsequently, the LC–PB-GDMS system was used to separate and identify the organic constituents in diet soda. We describe here the separation and identification of representative analytes of environmental and biological relevance. The ability to generate easily interpreted mass spectra from diverse inorganic, organic and organometallic species makes the PB/GD coupling unique among LC–MS detectors. Separations of four classes of compounds of much current interest, polycyclic aromatic hydrocarbons (PAHs), steroids, selenoamino acids, and alkyllead compounds are

presented here to illustrate the utility of the PB-GDMS system as a practical detector for LC separations of compounds of environmental and biological interest.

2. Experimental

2.1. Instrumentation

The PB-GDMS approach for LC detection was evaluated on an Extrel (Pittsburgh, PA, USA) Benchmark mass spectrometer system. The basic design of the LC–PB-GDMS instrumentation has been described previously [21], so only a brief description will be presented here. The solvent and analyte solutions pass from a Waters (Milford, MA, USA) Model 600S high-performance LC system, containing a Rheodyne (Cotati, CA, USA) 20-μl sample loop injector, through a stainless steel tube. The flow from the stainless tube can be directed into either a Waters UV absorbance detector (Model 2487) or the nebulizer of the particle beam apparatus. The Benchmark instrument is equipped with an Extrel Thermabeam particle beam interface, which consists of a thermoconcentric nebulizer to generate a finely dispersed aerosol, a heated (100°C) metal spray chamber for desolvation, and a two-stage momentum separator which removes residual solvent vapor and reduces the backing pressure. The resulting desolvated analyte particles (1–10 μm diameter) are introduced into the heated (~280°C) discharge volume, where they impinge on the cathode of the glow discharge, are vaporized, and the volatilized analyte species subsequently ionized.

The only substantive modification of the Benchmark system was the mounting of a glow discharge ion volume directly in the place of the commercial EI-chemical ionization (CI) source. The glow discharge electrode (a copper target) is mounted to the end of a direct insertion probe (DIP) [25] and inserted through the ''solids probe'' inlet into the ion volume assembly, perpendicular to the path of the incoming particles. Particles impinging on the electrode dissociate and diffuse into the plasma negative glow region, where they are ionized. The ionized analyte species are sampled through a 1-mm exit aperture to the quadrupole mass analyzer. The Benchmark mass spectrometer system operates under the control of a Sun SPARCstation (Sun Microsystems, Mountain View, CA, USA) using the Extrel IONstation software package. While the instrument is capable of both positive and negative ion analysis with a mass range of 2000 u, only positive ion detection was employed here. For the following separations, a 1 mA discharge current was generated by a Spellman high-voltage d.c. supply (Model RHR5N50, Plainview, NY, USA), while a constant discharge pressure of 810 mTorr Ar was employed (1 Torr=133.322 Pa). The Ar gas pressure was determined by a vacuum gauge (VRC Model 912011, Pittsburgh, PA, USA) connected to a pressure probe.

Due to the very limited output capabilities of the Benchmark MS system, mass spectra depicted throughout this paper take the form of histograms presented in MS Powerpoint (Microsoft, Seattle, WA, USA). To get into this format, the original mass spectra are recorded as two-dimensional text files, imported into MS Excel, and finally into Powerpoint. It must be mentioned that, while readily seen in the initial mass spectra generated by the MS data system, the combination of large dynamic range and limited mass resolution results in the loss of the expected ^{13}C isotope signatures in the final graphic production of many of the mass spectra.

2.2. Chromatographic columns, mobile phases, and samples

The analytical stationary phase used in most of this work was a 150 mm×3.9 mm I.D. column packed with C_{18} material (Novapak C_{18}; Waters). A longer (250 mm) and larger I.D. (4.6 mm) C_{18} column (Adsorbosphere C_{18}; Alltech, Deerfield, IL, USA) was employed for the steroid separation. For each separation, a different mobile phase composition was required with all solvents being reagent-grade quality (Fisher Scientific, Pittsburgh, PA, USA). The polyaromatic hydrocarbons were separated isocratically with an acetonitrile–water (75:25) combination, while the steroid separation employed a water–methanol (70:30) mobile phase. The selenoamino acid mixture was separated with water–methanol (95:5) with 0.1% trifluoroacetic acid (TFA; Aldrich, Milwaukee, WI, USA) in methanol. The

alkyllead species were separated by gradient elution with an initial mobile phase composition of methanol–water (40:60)–4 mmol sodium pentane sulfonate in water (pH 3). A gradient from 40 to 90% methanol over a period of 10 min was employed. Flow rates of 1.0 ml/min were employed for all of the separations except the selenoamino acids, where a 0.7 ml/min flow-rate was used.

Stock solutions of 150 ppm of the polyaromatic hydrocarbons (Aldrich) and the steroids (Sigma, St. Louis, MO, USA) were prepared with the appropriate mobile phase solvent composition. Aqueous stock solutions of 150 ppm of selenoamino acids (Sigma), steroids (Aldrich) and alkyllead compounds (Aldrich, and Alfa Aesar, Ward Hill, MA, USA) were prepared with HPLC-grade water. In order to dissolve the seleno-DL-cystine sample, 3% hydrochloric acid was added to the solution. Most of the analytical solutions were stored at room temperature, except for the selenoamino acids, which were refrigerated.

3. Results and discussion

3.1. Polycyclic aromatic hydrocarbons

To illustrate the capabilities for detection of PAHs, a simple isocratic separation of three PAHs was adapted from Anacleto et al. [26]. Due to the hydrophobicity of the low-molecular-mass PAHs, solutions were made with the mobile phase mixture containing the organic solvent in order to avoid the adsorption of the PAHs on the container walls [27]. Fig. 1a shows the resulting chromatogram obtained with UV absorbance detection at 254 nm. The corresponding separation with the PB-GDMS detection in the total ion chromatogram (TIC) mode is displayed in Fig. 1b. The retention times in each chromatogram are well correlated, with the peaks detected by PB-GDMS appearing ~1 min later than the UV due to the time required to traverse the additional tubing to the PB interface. These traces indicate that travel through the PB interface does not appear to contribute appreciably to peak broadening or tailing. Also interesting is the elution behavior of these smaller PAHs (M_r<300 u, pyrene, chrysene, and benzo[*a*]pyrene), which directly correlates to the molecular size and shape of the PAHs [28].

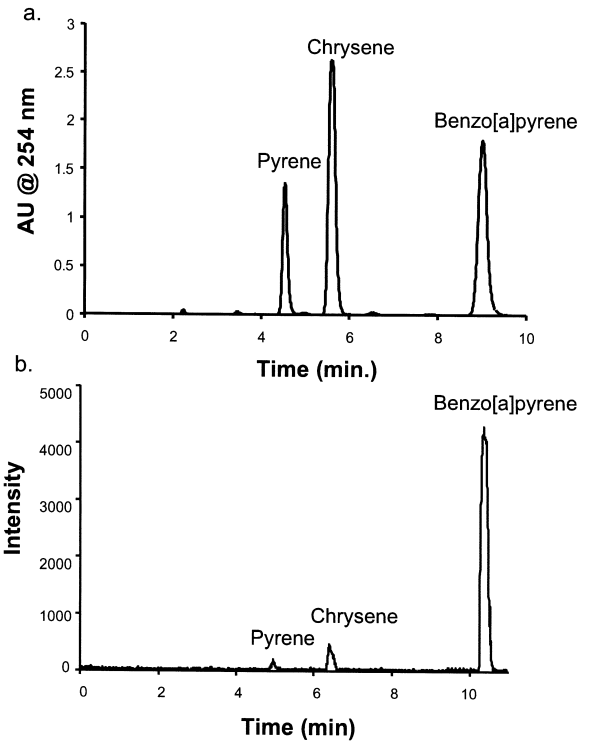

Fig. 1. HPLC separation of 150 ppm each of pyrene, chrysene, and benzo[*a*]pyrene. (a) UV detection at 254 nm and (b) PB-GDMS detection in TIC mode. Waters Novapak C_{18} column (150×3.9 mm); isocratic elution acetonitrile–water (75:25); flow-rate 1 ml/min; 20 μl injection.

Fig. 2a, b and c depict the individual glow discharge mass spectra obtained from the separation of pyrene (M_r=202), chrysene (M_r=228), and benzo[*a*]pyrene (M_r=252), respectively. As can be seen, the spectra are very simple in structure, with only the presence of the molecular ion. Thus the PB-GDMS spectra can be readily matched with those contained in EI mass spectral libraries. In fact, previous work using this same interface for direct particle introduction showed that substituted PAHs produced very easily interpreted mass spectra using the GD source described here [29]. The absence of eluent-related background ions is likely due to the fact that these species are sufficiently volatile that they are vaporized in the desolvation step and pumped away in the momentum separator. Previous LC–PB-MS work employing an EI source described by Pace and Betowski illustrate that simple mass spectra, con-

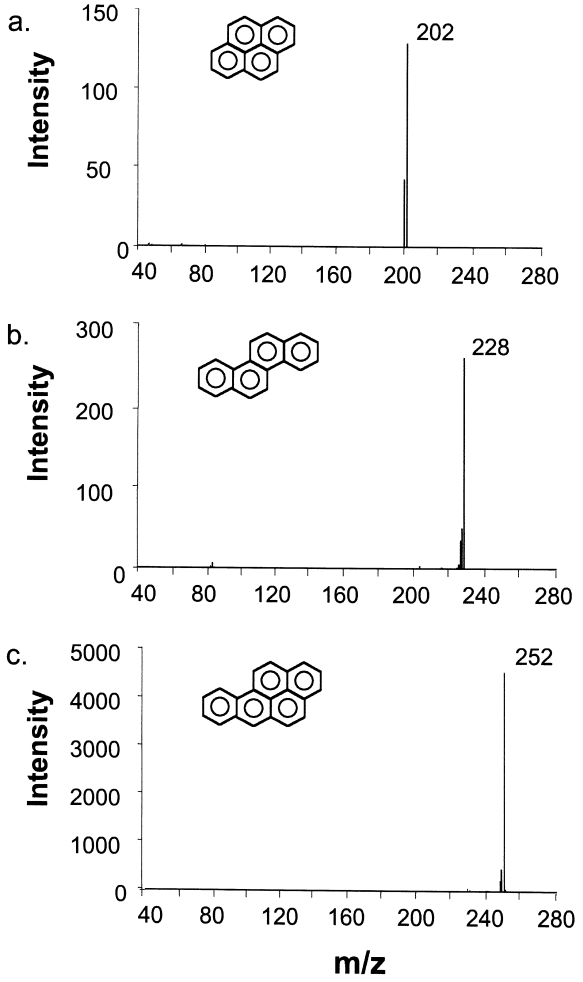

Fig. 2. Particle beam-glow discharge mass spectrum of 150 ppm (a) pyrene, (b) chrysene, and (c) benzo[*a*]pyrene. Ar discharge pressure=810 mTorr; discharge current=1.0 mA; 20 μl injection.

taining only singly and doubly charged molecular ions, could be obtained for high-molecular-mass PAHs (M_r>300 u) [28]. They determined the instrumentation detection limits to range from 10 to 54 ng in the scan/TIC mode for high-molecular-mass PAHs. In comparison, the signal-to-background ratios here suggest limits of detection (LODs) of the order of 30 ng.

3.2. Steroids

A simple isocratic separation for steroids was adapted from Ma and Kim [30]. The resulting

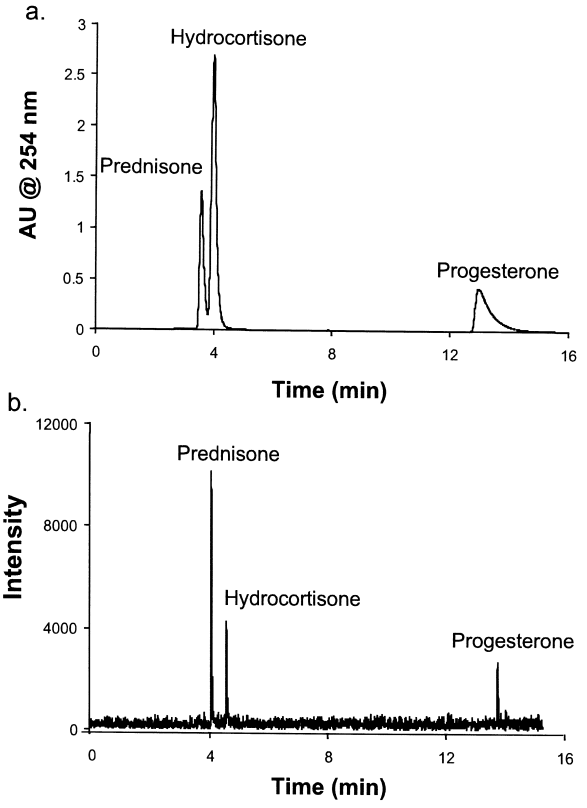

Fig. 3. HPLC separation of 150 ppm each of prednisone, hydrocortisone, and progesterone (a) UV detection at 254 nm and (b) PB-GDMS detection in TIC mode. Alltech Adsorbosphere C_{18} column (250×4.6 mm); isocratic elution methanol–water (70:30); flow-rate 1 ml/min; 20 μl injection.

chromatograms of the solutions with UV (254 nm) and MS (TIC mode) detection are shown in Fig. 3a and b, respectively. Similar retention times are observed when the ~1 min offset time to the PB interface is considered.

Fig. 4a, b and c depict the glow discharge mass spectra obtained from the separation of prednisone (M_r=358), hydrocortisone (M_r=362), and progesterone (M_r=314), respectively. Although the spectra are fairly complex, easily interpreted fragmentation patterns are observed for the three steroids. In the lower mass range (m/z<230 u), there are eleven similar fragments for this family of compounds. The possible structures of the characteristic ions of the fused ring structure have been considered here, with the suggested fragmentation locations shown in Fig.

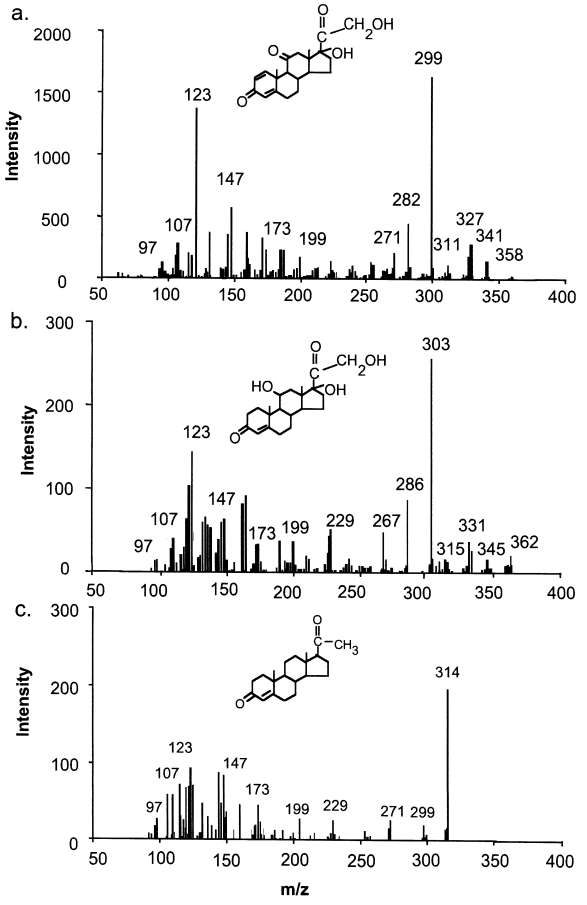

Fig. 4. Particle beam-glow discharge mass spectrum of 150 ppm (a) prednisone, (b) hydrocortisone, and (c) progesterone. Ar discharge pressure=810 mTorr; discharge current=1.0 mA; 20 μl injection.

5 for the specific case of prednisone. Each steroid spectrum contains the molecular ion, although it is not always the base peak of the spectrum. The more highly functionalized prednisone and hydrocortisone exhibit the loss of a hydroxyl group (M_r 341 and 345), formyl radical (HCO°) (M_r 327 and 331), and hydroxyacetyl radical ($COCH_2OH$°) (M_r 299 and 303) from the molecular ion in the PB-GDMS spectra. Other higher mass ions (M_r 286 and 282) are observed, indicating the removal of a hydroxyl radical from the most abundant ions in the mass spectra for prednisone and hydrocortisone, respectively. A similar ion fragmentation pattern is observed for the steroid, progesterone. There is a loss

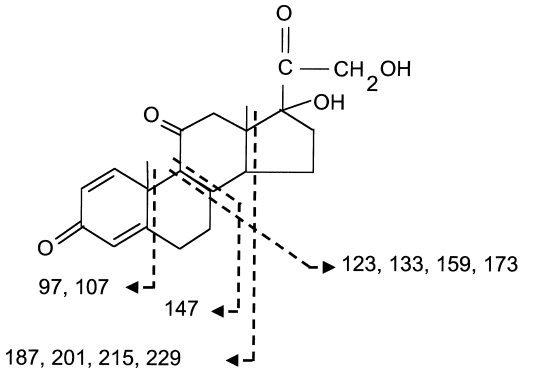

Fig. 5. Generalized low-mass fragmentation patterns for steroids.

of a methyl group (M_r 299) and the formyl radical (M_r 271), which compare well with the removal pattern of the other steroids. In general, classical EI sources show very similar fragmentation patterns for hydrocortisone and progesterone [31] (prednisone is not contained the NIST library), further indicating that the PB-GDMS spectra of organic compounds can be readily matched with those contained in EI mass spectral libraries. A direct comparison of sensitivity cannot be made for these steroids, since literature reports only involve the selected ion monitoring (SIM) monitoring mode (<1 ng) [32,33]. However, signal-to-background noise ratios in the TIC mode here suggest limits of detection on the order of 80 ng, which typically correlates with low nanogram levels in the SIM mode.

3.3. Selenoamino acids

Selenium is an essential element, which is nevertheless toxic in excess of the required trace levels. The toxicity, cancer chemo-activity and nutritional bioavailability of selenium have been found to be species dependent [34,35]. Thus, it is the chemical form of the selenium rather than the total concentration that determines the toxicity or bioavailability [35]. Therefore, it is important to identify and quantify the different species of selenium. There are various capabilities of ICP-MS detection which make the instruments valuable tools for elemental speciation in a wide variety of samples [34–36]; however, identification of selenium compounds with ICP-MS

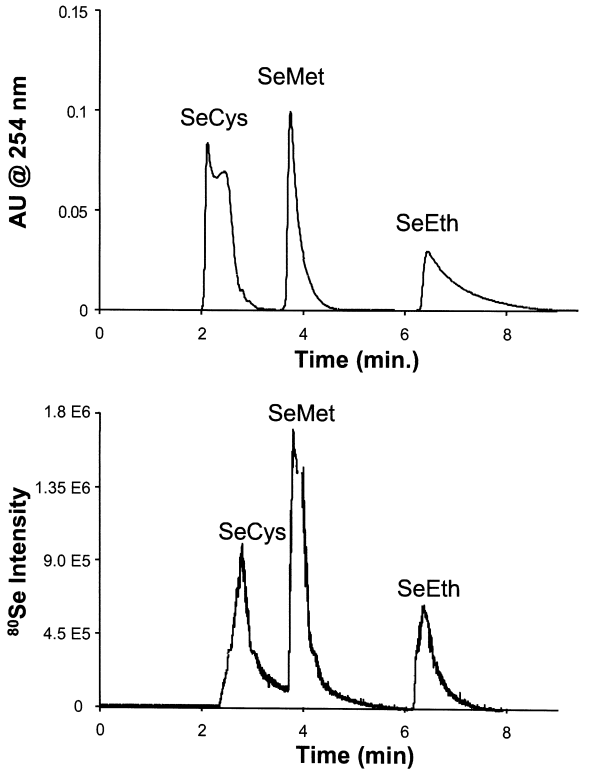

Fig. 6. HPLC separation of 150 ppm each of seleno-DL-cystine, seleno-DL-methionine, and seleno-DL-ethionine (a) UV detection at 254 nm and (b) PB-GDMS detection in SIM mode for $^{80}Se^{+}$ isotope. Waters Novapak C_{18} column (150×3.9 mm); isocratic elution water–0.1% TFA in methanol (95:5); flow-rate 0.7 ml/min; 20 μl injection.

is based solely on their retention characteristics. The lack of available standards to identify the selenium compounds with ICP-MS, requires the use of supplementary techniques such as molecular mass spectrometry via PB/EI or electrospray for identification of unknown compounds in natural sample extracts.

Fig. 6a and b show the chromatograms for three selenoamino acids with UV (254 nm) and PB-GDMS (SIM mode of the $^{80}Se^{+}$ isotope) detection, respectively. The separation conditions for 150 ppm each of selenocystine (SeCys), selenomethionine (SeMet), and selenoethionine (SeEth) were adapted from Puskel et al. [37]. The concentrations of methanol and TFA in the eluent were optimized by Puskel et al. [37] and further by Pearson and McCroskey [38]. Although a 1.0 ml flow-rate yielded better overall peak shapes, a 0.7 ml flow-rate was employed to minimize the overlap of the SeCys and SeMet peaks. The separation shown in Fig. 6b is fairly good, with minimal overlap of the SeCys and SeMet peaks. A similar overlap was demonstrated by Puskel et al. [37].

As mentioned previously, most speciation techniques do not provide both elemental and molecular information. Shown in Fig. 7a, b and c are the glow discharge mass spectra obtained for the flow injection analysis of SeCys (M_r=336), SeMet (M_r=197), and SeEth (M_r=211), respectively. Although the spectra exhibit a large number of product ions, straightforward fragmentation patterns are observed for the selenoamino acids. All three contain the ion fragments of 80, 95, and 109, representing the elemental Se, methylated Se, and ethylated Se ion fragments, respectively. Masses 123 and 124 are also similar for the three organometallic compounds, with the difference being the substitution of a N for a CH group in the SeCys spectrum. The SeCys spectrum contains only one other fragment, which depicts the ion fragment where the molecule is cleaved (in half) at the Se to Se bond. The other two compounds' mass spectra parallel one another and display the deprotonated molecular ion, as well as the loss of a methane and carboxylic acid group. Kotrebai et al. LC–ion trap (IT) MS with an electrospray ionization source as a qualitative method to complement their LC–ICP-MS analysis of biological extracts [39]. In those studies, LC–ICP-MS detection limits of ~1 ng were obtained. In comparison, the signal-to-background ratios for these SIM data suggest comparable limits of detection, on the order of 5 ng. It should be noted that there does exist a range of discharge operating conditions which in principle could be employed to elicit greater or lesser amounts of fragmentation (i.e., atomic ion contributions, etc.). Even so, the typical precision of the experiments to date (5% RSD), suggests that the plasma itself operates quite stably with respect to the ionization processes. The role of discharge conditions on the observed degree of fragmentation will be the topic of a future study.

3.4. Alkyllead compounds

Tetraalkyllead compounds and their degradation products (trialkyllead compounds) are the dominant

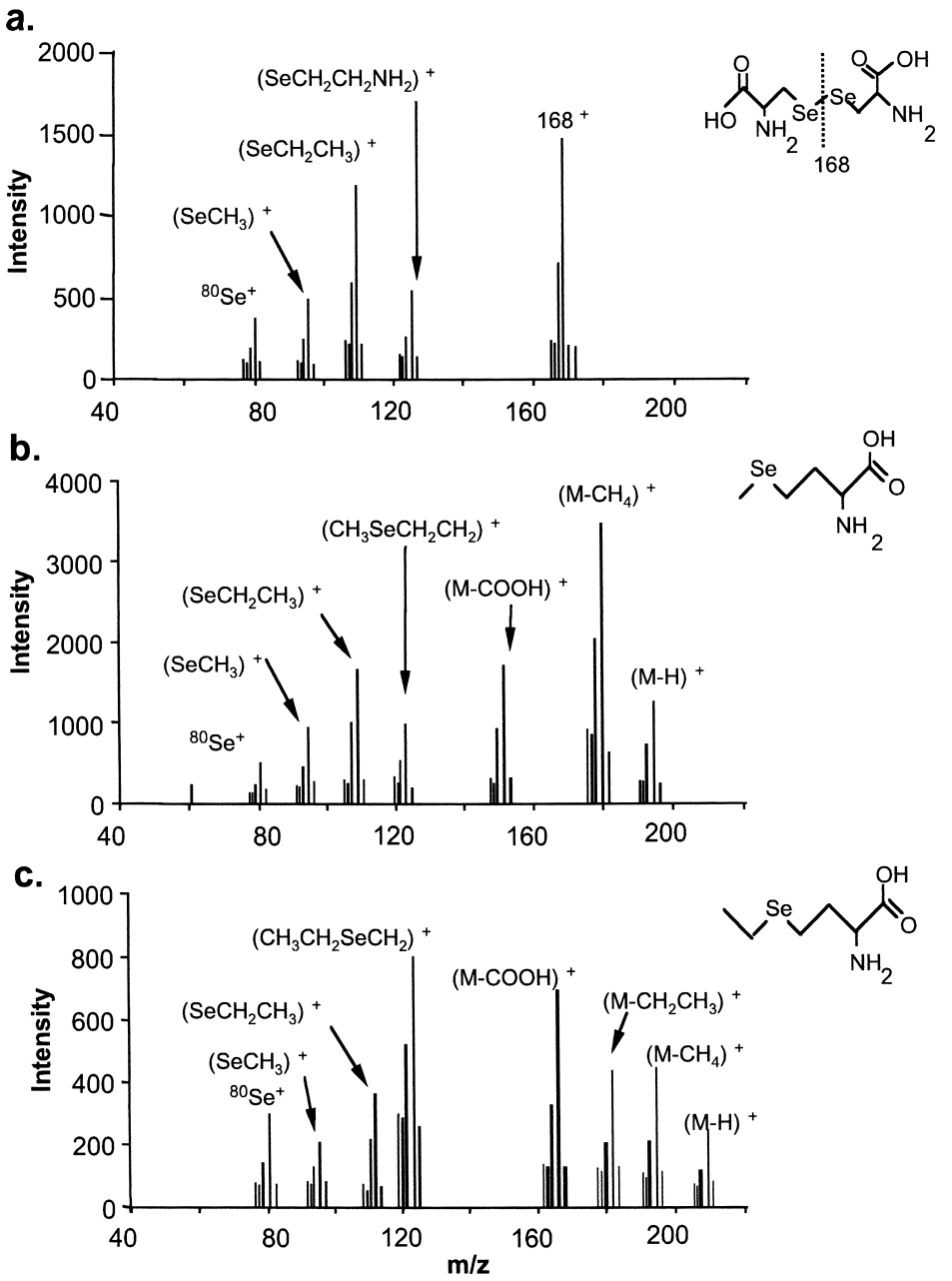

Fig. 7. Particle beam-glow discharge mass spectrum of 150 ppm (a) seleno-DL-cystine, (b) seleno-DL-methionine, and (c) seleno-DL-ethionine. Ar discharge pressure=810 mTorr; discharge current=1.0 mA; 20 μl injection.

source of lead environmental contamination [40]. For this reason, speciation of molecular and ionic alkyllead compounds has become necessary to determine their toxicity and environmental consequences. For this study, a gradient separation of alkyllead compounds was adapted from Al-Rashdan et al. [41]. Fig. 8a and b show the chromatograms for the three lead species [150 ppm each of lead nitrate,

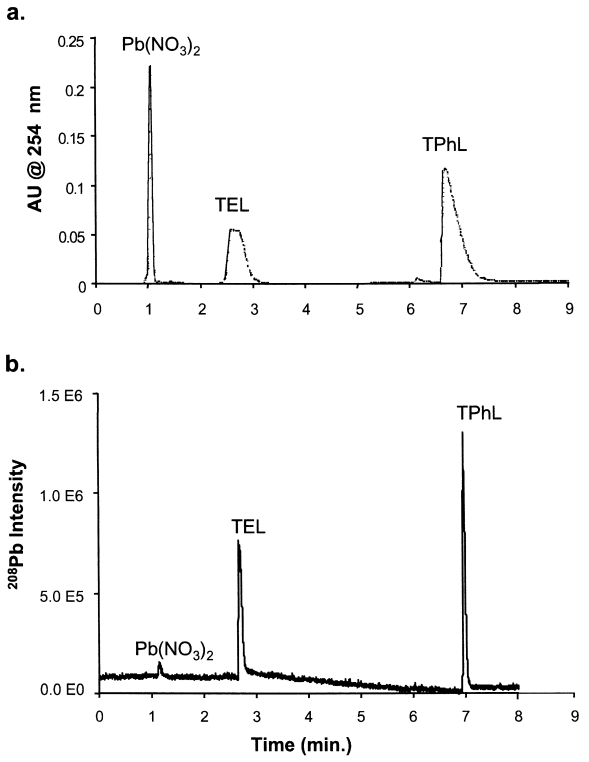

Fig. 8. HPLC separation of 150 ppm each of lead nitrate [$Pb(NO_3)_2$], triethyllead chloride (TEL), and triphenyllead chloride (TPhL) (a) UV detection at 254 nm and (b) PB-GDMS detection in SIM mode for $^{208}Pb^+$ isotope. Waters Novapak C_{18} column (150×3.9 mm); 4 m*M* 1-pentanesulfonic acid, sodium salt at pH 3.0 pairing agent, gradient elution 40 to 90% methanol over 10 min; flow-rate 1.0 ml/min; 20 μl injection.

triethyllead chloride (TEL), and triphenyllead chloride (TPhL)] with UV absorbance (254 nm) and PB-GDMS (SIM mode of the $^{208}Pb^+$ isotope) detection, respectively. Similar retention times are present when the ~1 min offset for the PB interface is incorporated. The LC–ICP-MS study by Al-Rashdan et al. resulted in an identical elution order of the three lead compounds, however, only sufficient resolution between lead nitrate and TEL was obtained due to peak tailing of the lead nitrate [41]. As can be seen in Fig. 8b, complete resolution of the three components was obtained with GDMS detection.

Fig. 9a, b and c depict the glow discharge mass spectra obtained for the flow injection analysis of lead nitrate (M_r=332), TEL (M_r=330), and TPhL (M_r=474), respectively. As can be seen, the lead nitrate spectrum is very simple, containing only the isotopic distribution for elemental Pb. The mass spectra of the alkyllead compounds (Fig. 9b and c) also contain the elemental Pb isotope pattern, as well as a lead chloride (i.e., metal–counterion pair) signature in the region of 243 u and specific ion fragments related to their molecular structure. The TEL spectrum (Fig. 9b) shows not only the molecular ion, but also sequential losses of the ethyl groups to form fragments at 267 and 237 u. In the TPhL spectrum the molecular ion is not present, there is a fragment for a phenyl-substituted Pb at 285 u, as well as a large presence of the phenyl and biphenyl ions at 77 and 154 u, respectively. Thus, implying that the TPhL species is not stable under the GD conditions employed here. In fact, the production of the bi-phenyl ions is characteristic of these sorts of compounds in photolysis studies of metal aryls in benzene solvent [42]. Similarly, biphenyl is an observed product in the photolysis of perphenyl compounds when carbon is the central atom [43]. Even so, it is not hard to extrapolate the fact that the molecule is composed solely of phenyl substituents and not other alkyl functionalities, as these would be present in the spectrum. Thus, the LC–PB-GDMS technique provides not only the detection of the metal, but also ligand information, allowing identification of the original species.

To further characterize the PB-GDMS detection for LC analysis of these organometallic compounds, Table 1 shows the calibration data for the ^{208}Pb isotope response in the three compounds, as well as the molecular ion for TEL (m/z=295 u). These data illustrate the capability of the PB-GDMS technique for the quantitative determination of both metals and organic species. For this study, the average integrated area of triplicate injections over a concentration range of 10 to 200 ppm Pb were fit to a linear least-squares calibration response. In each instance, the RSD was less than 4%. As can be seen, the sensitivity of the ^{208}Pb isotope response in the three compounds improves with the species volatility (i.e. melting points: lead nitrate=470°C, TEL=120°C (decomposition), and TPhL=270°C). This trend is also observed in the detection limits, which were computed by multiplying the standard deviation of the background signal prior to the first injection by 3

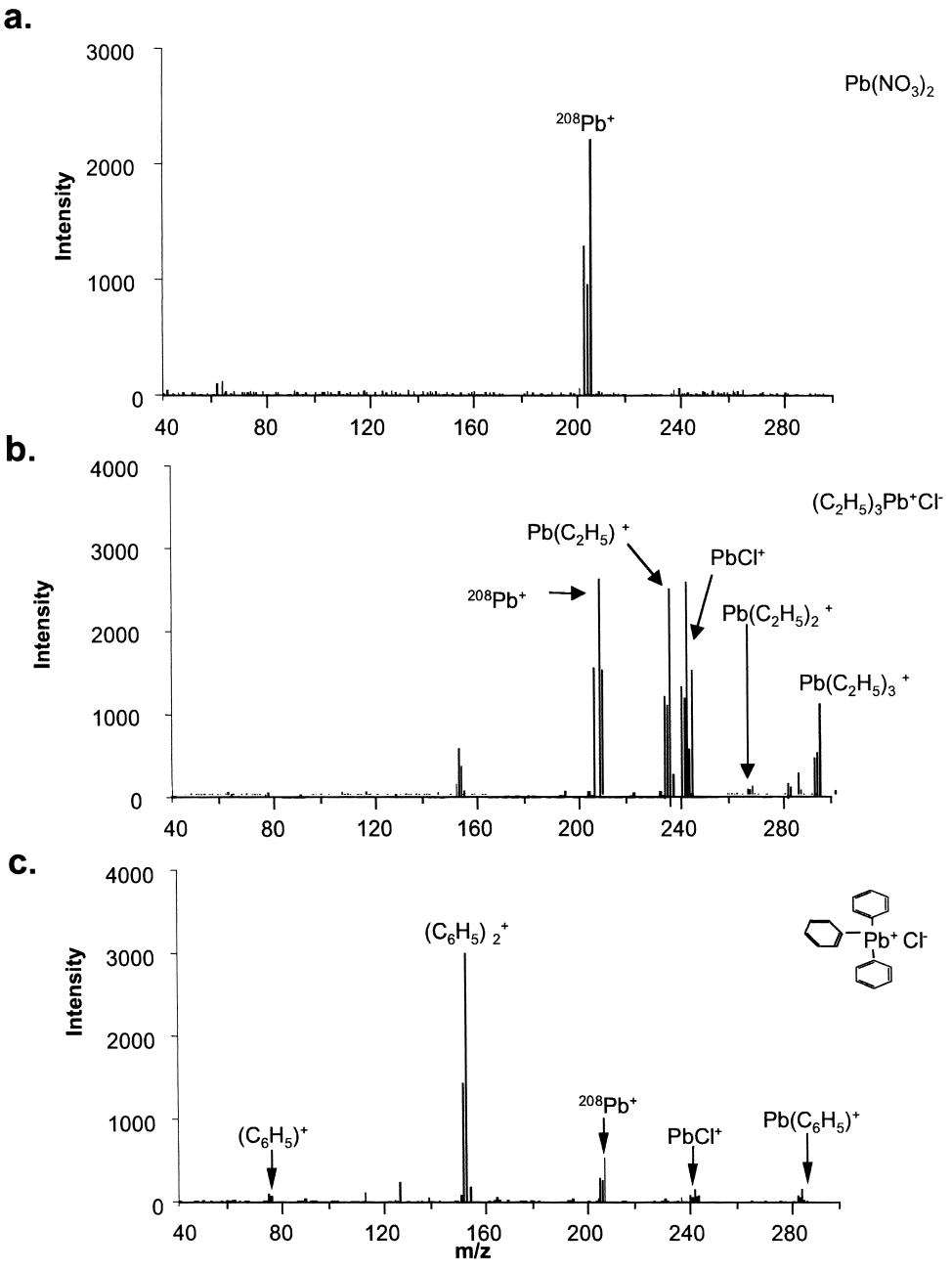

Fig. 9. Particle beam-glow discharge mass spectrum of 150 ppm (a) lead nitrate, (b) triethyllead chloride, and (c) triphenyllead chloride. Ar discharge pressure=810 mTorr; discharge current=1.0 mA; 20 μl injection.

and dividing by the slope of the calibration functions (LOD=$3\sigma_{bckgnd}$/slope). Detection limits for the ^{208}Pb isotope in lead nitrate, TEL, and TPhL were 2.98, 0.82, and 0.18 ng Pb, respectively. In a similar manner, the detection limit of 26 ng TEL (19 ng Pb) was calculated based on the response of the TEL molecular ion. The ^{208}Pb detection limits compare well with those obtained by ICP-MS by Al-Rashdan

Table 1
Analytical response characteristics for alkyllead species by PB-GDMS[a]

Analyte/matrix	Response function	R^2	Detection limit as Pb
$^{208}Pb/Pb(NO_3)_2$	$y=327\,658x-7\cdot10^6$	0.944	150 ppb Pb (3 ng Pb)
$^{208}Pb/TEL$	$y=684\,524x-1\cdot10^7$	0.982	40 ppb Pb (0.8 ng Pb)
$^{208}Pb/TPhL$	$y=2\cdot10^6x-2\cdot10^7$	0.995	9 ppb Pb (0.2 ng Pb)
^{295}TEL	$y=16\,691x-278\,391$	0.975	980 ppb Pb (19 ng Pb)
			1 ppm TEL (26 ng TEL)

[a] Test range 100 ppb–200 ppm, five data points for each calibration curve.

et al. [41] who obtained values of 0.14–0.37 ng. However, the explicit nature of the inductively coupled plasma to totally dissociate all analyte species limits the analysis of molecular species, thus a comparison for the molecular ion detection limit is not available. In general, each species produced linear calibration results with good regression coefficients and sensitivity.

4. Conclusions

The potential of the PB-GDMS coupling as a practical detector for LC has been demonstrated. Chromatographic separation characteristics display good correlation between UV and PB-GDMS detection modes for both organic and organometallic compounds of environmental and biological interest. Mass spectra for the biological and environmental species illustrate the capability of both inorganic (metals) and organic (molecular) analysis, indicating the utility of this technique for true speciation. LC–PB-GDMS provides both the metal and ligand information, allowing full identification of the species. Encouraging analytical response curve characteristics were obtained for both the elemental lead in the three compounds and the molecular ion for one alkyllead molecule, suggesting the quantitative use of this technique for the analysis of both elemental and molecular species. Future work will focus on implementing a hollow cathode discharge design [22], which should result in more efficient vaporization and overall ionization, thus improving the overall sensitivity of this technique. Although further work is required to optimize this technique for real-world analysis, these studies demonstrate the promise of the PB-GDMS system as a practical detector for LC.

Acknowledgements

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